

# CATALYSTS SYNTHESIZED BY ATOMIC LAYER DEPOSITION FOR PARTIAL OXIDATION OF ALKANES

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## INTRODUCTION

Atomic Layer Deposition (ALD) is a thin film growth technique that uses alternating cycles of saturating reactions between gaseous precursor molecules and a substrate to deposit films in a monolayer by monolayer fashion (1). ALD can also be applied as a flexible way to synthesize catalytic structures since most catalytically active materials can be deposited using this method. In ALD the gaseous diffusion of the reactive precursors, along with self-termination of the individual chemical reactions ensure that all surfaces are coated uniformly even in the case of high surface area nanoporous solids. The uniformity of the catalytic materials synthesized by ALD will reduce the typical complexity and inhomogeneity of heterogeneous catalysts and thereby enhance our fundamental understanding of composition/structure/ function relationship in supported heterogeneous catalysts. In alkane partial oxidation reactions, it has been shown that the selectivity to the partial oxidation products relies largely on the catalyst domain size (2). The layer by layer deposition fashion of ALD enables the synthesis of well-defined sub-nanometer scale catalytic clusters, which would potentially improve the selectivity to partial oxidation products in these reactions.

## EXPERIMENTAL

The performances of ALD vanadium oxides catalysts were studied in the oxidative dehydrogenation (ODH) of cyclohexane. The substrate used in this reaction is a nano-structured anodic aluminum oxide (AAO) monolith. Detailed descriptions about the synthesis of the catalytic nanolith can be found in (3). In brief, before loading catalytic materials onto the as-prepared nanolith, approximately 1 nm of Al<sub>2</sub>O<sub>3</sub> was coated onto the AAO by ALD to completely cover electrolyte impurities incorporated into the oxide material during anodization. Alumina ALD was carried out at 200°C in a viscous flow reactor (4). Ultra high purity nitrogen was used as the purge gas. The layer-by-layer growth of alumina was achieved by alternatively exposing the AAO substrates to trimethyl aluminum and water for 8 cycles using a quasi-static reactor operation mode in which the reactor is pumped down to 0.1 torr after each dose and purge. Vanadium oxide catalytic material (VOx) was then introduced by ALD using a procedure similar to that reported by Keranen etc. (5), in which the AAO was exposed to vanadyl oxytriisopropoxide and hydrogen peroxide/water. A dosing/purging timing sequence of 45-30-45-30 s was used to deposit layer(s) of VOx onto the AAO structure at 100°C, 1.1 Torr, with a

nitrogen flow rate of 240sccm/min.

Catalytic reactions were performed in an ALD-alumina-coated stainless steel reactor modified from a standard Swagelok VCR fitting, in which the gasket was replaced by the nanolith system. Cyclohexane vapor was introduced into the reaction system using a helium bubbler. The reactant gas was made up of 1% cyclohexane, 2% oxygen, and 97% helium. The total flow rate through the reactor was 10 sccm/min. The oxidation reaction was carried out at temperatures between 400°C and 480°C at atmospheric pressure.

## RESULTS

In the ODH reaction of cyclohexane, the nanoliths loaded with the ALD VOx show much higher TOF than those with the impregnated VOx, which reflects the better dispersion of the catalytic species as synthesized by ALD. With increasing loading of the catalyst, the ALD samples exhibit a rising tendency in the catalytic activity while the activities of the wet impregnated samples remain unchanged. UV-Vis studies show that the supported VOx are in the isolated state at low V loadings; polyvanadate domains gradually form as the number of VOx ALD cycles increases. Therefore the polyvanadate sites are more active than the monovanadate sites in the ODH of cyclohexane. On the other hand, the isolated VOx are shown to be more selective to the olefin than the polymeric VOx. By comparing the ODH of cyclohexane and the oxidations of cyclohexene and benzene, we find that both the sequential path and the parallel path (the direct conversion from cyclohexane to benzene) exist in the oxidation process of cyclohexane. The formation of benzene may go through either the sequential path or the parallel path, depending on the structure of the VOx catalyst.

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